



Enthalpies of solution and partial molar volumes of magnesium perchlorate in alcohols and salt effect of acceleration of the Diels–Alder reaction

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ABSTRACT

Densities and enthalpies of solution at 25 °C were measured for dilute solutions of magnesium perchlorate (MP) in some alcohols using the Anton Paar DSA 5000M vibrating tube densimeter and differential calorimetric measurements. In all studied solvents the solution of MP was highly exothermic and large solvent volume contraction was observed. Maximum effect was obtained in methanol and ethanol solutions. Acceleration effect of the Diels–Alder reaction of 9,10-dimethylanthracene with acrylonitrile in the medium of acrylonitrile in the presence of salts LiClO_4 , $\text{Mg}(\text{ClO}_4)_2$ and GaCl_3 was as 18:160:59,000.

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1. Introduction

Perchlorates of alkali and alkaline earth metals have high solubility in polar *n*-donor aprotic and protic mediums. Metal ions are stabilized by the strong interaction with the *n*-donor centers of the solvent molecules, and the large size perchlorate anion, possessing a high degree of delocalization of the charge, is stabilized by the interaction with polar solvent [1–3]. At present there is a large database on the heats of solution and partial molar volumes (PMV) of salts in water and some organic solvents [4–7]. Increased scatter of literature data on these parameters is more often observed for solvents with low dielectric constant, ϵ , and/or low donor numbers, *DN*. Since the limiting concentration of calorimetric measurements typically $\sim 10^{-3} \text{ mol L}^{-1}$, and in the measurements of the molar volume of $\sim 10^{-2} \text{ mol L}^{-1}$, the complete dissociation of salts in these conditions is not always observed, and extrapolation to zero concentration can lead to appreciable errors. For lithium [6] and magnesium [7] perchlorates it was showed that the dissolution of anhydrous salts in solvents, accompanied by a strong exothermic effect, and the values of PMV sharply decrease due to electrostriction and even may be negative. For magnesium perchlorate it was noted more dramatic change of these characteristics than for lithium perchlorate (LP) [7]. In relation to our systematic

study of the salt effects on reaction rate [8–10], partial molar volumes and enthalpies of solution of salts in organic solvents [6], the properties of magnesium perchlorate in alcohols (methanol, ethanol, propanol-1, propanol-2, butanol-1, 3-methylbutanol-1 and hexanol-1) were studied in this work. Acceleration effect of the Diels–Alder reaction in the presence of MP was estimated and compared with that of LP and gallium chloride.

2. Experimental part

2.1. Materials

Magnesium perchlorate “trihydrate” (Fisher Scientific), typically a sample of 7–10 g in a glass vessel, had an initial water content about 15% and was dried in a glass tube at 240–245 °C for 20–25 h in vacuum ($\sim 50 \text{ Pa}$). The tube (50 cm) with freshly dried calcium chloride was connected between a sample with MP and vacuum pump. For a high efficiency of drying, the growth of the melting point of the sample MP should be higher than the elevation of temperature of the heater. Smooth elevation of the temperature up to 245 °C of the heater was carried out for about 6 h. The holding of the vessel with the MP sample under these conditions (240–245 °C, 50 Pa, 20–25 h) to the constant weight ($\pm 2 \text{ mg}$) is an accurate (>99.9%) testing method of the final dehydration.

Spectral purity of 9,10-dimethylanthracene (Aldrich, mp 182–183 °C, lit. 183–184 [11]) was obtained after column chromatography (eluent benzene:*n*-hexane, 1:5) and was confirmed

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